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[Title of the Invention] ADDITIVE FOR SELF-LEVELING MATERIAL

[Abstract]

[Problem] To provide an additive that is used for self-leveling materials, excellent in the surface smoothness and the adhesion strength to substrates and capable of reducing generation of the cracks accompanying expansion or contraction.

[solving Means] An additive for self-leveling materials includes, as an essential ingredient, a water-soluble copolymer that is obtained by polymerizing a monomer mixture containing one or more kinds of (a) vinyl monomers including compounds each having a polyoxyalkylene chain obtained by adding alkylene oxide having 2 to 3 carbon atoms at an average addition mole number of 60 to 300; and one or more kinds of (b) vinyl monomers including a compound having a carboxyl group, a sulfonic group or an amide group or a water-soluble salt thereof.

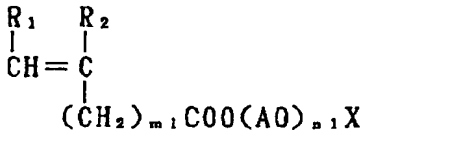
[Scope of Claim for a Patent]

[Claim 1] An additive for a self-leveling material including, as an essential ingredient, a water-soluble copolymer that is obtained by polymerizing a monomer mixture containing one or more kinds of (a) vinyl monomers including a compound having a polyoxyalkylene chain obtained by adding alkylene oxide having 2 to 3 carbon atoms at an average addition mole number of 60 to 300; and one or more kinds of (b) vinyl monomers including a compound having a carboxyl group, a sulfonic group or an amide group or a water-soluble salt thereof.

[Claim 2] An additive for a self-leveling material as set forth in claim 1:

wherein the monomer (a) is a compound expressed by a general formula (I), and the monomer (b) is a compound expressed by a general formula (II) or (III).

[Ka 1]

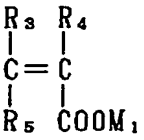


(I)

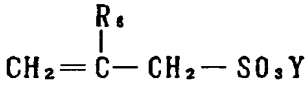
(In the formula, R_1 and R_2 each denote simultaneously or separately a hydrogen atom or a methyl group; m_1 is an integer of 0 to 2; AO, an oxyalkylene group having 2 to 3 carbon atoms; n_1 is a number of 60 to 300 that denotes an average addition mole number of alkylene oxide; and X is a hydrogen atom or an alkyl group having 1 to 3 carbon

atoms.)

[Ka 2]



(II)



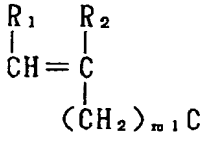
(III)

(In the formulas, R_3 denotes a hydrogen atom or a methyl group; R_4 and R_5 each, simultaneously or separately a hydrogen atom, a methyl group or $-(CH_2)m_2COOM_2$; R_6, a hydrogen atom or a methyl group; M_1, M_2 and Y, simultaneously or separately a hydrogen atom or a positive ion group; and m_2 is an integer of 0 to 2. When R_4 or R_5 is $-(CH_2)m_2COOM_2$, an anhydride may be formed.)

[Claim 3] An additive for a self-leveling material as set forth in claim 1 or 2:

wherein a monomer mixture further contains a monomer (c) expressed by a general formula (IV) below.

[Ka 3]



(IV)

(In the formula, R_1, R_2, m_1, AO and X each denote the

aforementioned meanings, and n_2 is a number of 2 to 40 that denotes an average addition mole number of alkylene oxide.)

[Claim 4] An additive for a self-leveling material as set forth in any one of claims 1 through 3:

wherein a ratio of a monomer (a), a monomer (b) and a monomer (c) in a monomer mixture is, by mole ratio, [monomer (a) + monomer (c)]/monomer (b) = 0.1/100 to 200/100.

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to an additive that is used for self-leveling materials and exhibits excellent effects in the smooth finishing and the adhesive strength to a substrate and reduction of the crack generation accompanying expansion or contraction.

[0002]

[Prior Art and Problems that this Invention is to Solve]

So far, in finishing an uneven floor surface such as concrete slab and so on, it is general to lay mortar on slab followed by applying trowel finishing by a plasterer to finish with smoothness; however, in finishing by manpower, there are problems in that many plasterers are necessary and working efficiency is poor. Contrary to this, in the case of the self-leveling material, by use of mortar slurry excellent in the fluidity, the finishing is

carried out owing to a natural flowing action; though it is advantageous in that high efficiency applications can be applied, there are disadvantages in that the surface smoothness is poor, the adhesive strength to the substrate is poor and so on.

[0003] In general, in the self-leveling material, a dispersing agent for improving the fluidity and a viscosity improver for suppressing material from separating are blended. As one example of the dispersing agents, melamine sulfonic acid-formalin condensate salts and naphthalene sulfonic acid-formalin condensate salts can be cited. Furthermore, as the viscosity improver, non-ionic cellulose ether can be used. As one example thereof, methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose and so on can be cited. However, in these conventional dispersing agents, since a larger addition amount is necessary to improve the fluidity, the hardening of hydraulic cement and gypsum is retarded. Furthermore, also the retarding properties of the viscosity improver that is added to improve the separation resistance are added thereto; accordingly, the material separation and generation of bleeding water due to retardation in the coagulation are considered to be factors that deteriorate the smoothness of a hardened surface. Furthermore, there are demands for additives that are also effective in improving the adhesive strength to the substrate and in reducing the generation of cracks.

[0004] In recent years, as a dispersing agent that can improve the fluidity of the self-leveling material and can render an influence of the retarding properties less, a water-soluble vinyl polymer having an oxyalkylene group is proposed (Japanese Patent Application Publication (JP-B) No. 64-1425 and Japanese Patent Application Laid-open (JP-A) No. 09-309756). However, even the use of these dispersing agents is insufficient in the effect; accordingly, there still remain problems in the surface smoothness, the adhesive strength to a substrate, the cracks and so on.

[0005]

[Means for Solving the Problems]

The present invention is an additive that is used for self-leveling materials and includes, as an essential ingredient, a water-soluble copolymer that is obtained by polymerizing a monomer mixture containing one or more kinds of (a) vinyl monomers made of a compound that has a polyoxyalkylene chain obtained by adding alkylene oxide having 2 to 3 carbon atoms at an average addition mole number of 60 to 300; and one or more kinds of (b) vinyl monomers made of a compound having a carboxyl group, a sulfonic group or an amide group or a water-soluble salt thereof.

[0006] When effects of the additive according to the invention are considered from a structure thereof, it is supposed that a polyoxyalkylene chain in the water-soluble

copolymer is involved in the appearance and maintenance of the fluidity and the adhesive strength to the substrate, and the water-retention capability of the polyoxyalkylene chain effectively works. That is, it was found that in order to inhibit, owing to the fluidity and the water-retention capability of the polyoxyalkylene chain, the bleeding water from being generated, a chain length of the polyoxyalkylene chain is important; ones disclosed in JP-B-64-1425 and having an addition mole number of alkylene oxide of 30 or less and ones disclosed in JP-A-09-309756 and having an addition mole number of alkylene oxide of 50 or less are insufficient in the fluidity and the suppression effect of the bleeding water, and when an average addition mole number of alkylene oxide is 60 or more, an advantageous effect can be displayed.

[0007]

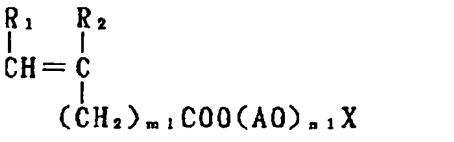
[Modes for Carrying out the Invention]

The monomer (a) according to the invention has a polyoxyalkylene chain in which alkylene oxides having 2 to 3 carbon atoms are added at an average addition mole number of 60 to 300 and thereby is excellent in the surface smoothness and the adhesive strength to the substrate. However, when the average addition mole number exceeds 300 or is less than 60, the surface smoothness and the adhesive strength are unfavorably deteriorated. The average addition mole number of alkylene oxide is particularly preferable in the range of 100 to 200.

[0008] As the alkylene oxides having 2 to 3 carbon atoms, ethylene oxide and propylene oxide can be cited, ethylene oxide being particularly preferable. An addition mode of these alkylene oxides may be any one of a single addition of one kind of alkylene oxides, or a random addition, a block addition and an alternate addition of two or more kinds. As the monomer (a), compounds represented by the following general formula (I) can be cited.

[0009]

[Ka 4]



(I)

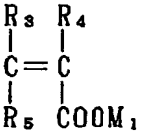
[0010] (In the formula, R_1 and R_2 each denote simultaneously or separately a hydrogen atom or a methyl group; m_1 is an integer of 0 to 2; AO, an oxyalkylene group having 2 to 3 carbon atoms; n_1 is a number of 60 to 300 that denotes an average addition mole number of alkylene oxide; and X is a hydrogen atom or an alkyl group having 1 to 3 carbon atoms.) As specific examples of compounds that are represented by the general formula (I), ester compounds between polyalkylene glycols having alkyl-blocked one end such as alkoxy polyethylene glycol, alkoxy polyethylene polypropylene glycol and so on and acrylic acid or methacrylic acid; and ethylene oxide and/or propylene oxide adducts to acrylic acid or methacrylic

acid can be cited, the former ester compounds being preferably cited.

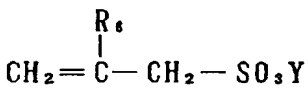
[0011] The monomers (b) include compounds having a carboxyl group, a sulfonic group or an amide group or water-soluble salts thereof. As the water-soluble salts, metal salts such as sodium salts, potassium salts, calcium salts, magnesium salts and so on, ammonium salts, triethanolamine salts, diethanolamine salts, monoethanolamine salts and so on can be cited. As the monomers (b), compounds represented by general formulas (II) and (III) can be cited, compounds represented by the general formula (II) being preferable.

[0012]

[Ka 5]



(II)



(III)

[0013] (In the formula, R_3 denotes a hydrogen atom or a methyl group; R_4 and R_5 each, simultaneously or separately a hydrogen atom, a methyl group or $-(CH_2)m_2COOM_2$; R_6, a hydrogen atom or a methyl group; M_1, M_2 and Y, simultaneously or separately a hydrogen atom or a positive ion group; and m_2 is an integer of 0 to 2. When R_4 or R_5

is $-(CH_2)m_2COOM_2$, an anhydride may be formed.)

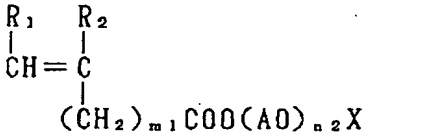
As specific examples of the compounds represented by the general formula (II), unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid and so on; unsaturated dicarboxylic acids such as maleic acid, itaconic acid, citraconic acid, fumaric acid and so on or anhydrides thereof; alkali metal salts of these carboxylic acids; alkali earth metal salts thereof; ammonium salts thereof; amine salts thereof and so on can be cited.

[0014] Furthermore, as specific examples of the compounds represented by the general formula (III), allyl sulfonic acids, methallyl sulfonic acids or alkali metal salts thereof, alkali earth metal salts thereof, ammonium salts thereof, amine salts thereof and so on can be cited.

[0015] Still furthermore, a monomer mixture involving the invention may further contain, other than the above monomers (a) and (b), a monomer (c) represented by the following general formula (IV).

[0016]

[Ka 6]



(IV)

[0017] (In the formula, R_1, R_2, m_1, AO and X each denote the aforementioned meanings, and n_2 is a number in the

range of 2 to 40 that shows an average addition mole number of alkylene oxide.)

In the case of a monomer mixture that contains the monomer (c) being used, a compound in which n_1 in the general formula (I) is in the range of 100 to 200 and a compound in which n_2 in the general formula (IV) is in the range of 5 to 30 are preferably used. Furthermore, a mixing ratio of these is, by eight ratio, preferably in the range of monomer (a)/monomer (b) = 10/90 to 90/10.

[0018] A copolymer involving the invention can be manufactured by polymerizing the monomer mixture according to a known method such as a solvent polymerization method and so on disclosed in, for instance, JP-A-07-223852. For instance, the above monomer mixture need only be reacted in water or a lower alcohol having 1 to 4 carbon atoms, in the presence of a polymerization initiator such as ammonium persulfate, hydrogen peroxide and so on, as needs arise by adding hydrogen sodium sulfite, mercaptoethanol and so on, in a nitrogen atmosphere at a temperature in the range of 50 to 100 degree centigrade for 0.5 to 10 hr.

[0019] In a range that does not disturb effects of the invention, another copolymerizable monomer may be further copolymerized. As examples of such monomers, acrylonitrile, acrylamide, methacrylamide, styrene and so on can be cited.

[0020] As to a ratio by mole of the monomers (a), (b) and (c) that constitute a copolymer, a range of [monomer (a) +

monomer (c)]/monomer (b) = 0.1/100 to 200/100 is preferable because of excellent surface smoothness and the adhesive strength to the substrate, in particular a range of [monomer (a) + monomer (c)]/monomer (b) = 5/100 to 100/100 being preferable. Furthermore, a total content of the monomers (a), (b) and (c) in the monomer mixture that constitutes the copolymer is preferably 50% by weight or more, and particularly preferably 80% by weight or more.

[0021] A weight average molecular weight of the copolymer (gel permeation chromatography/in terms of reference substance of polystyrene sodium sulfonate/water) is preferably in the range of 5,000 to 500,000 because of excellent surface smoothness and the adhesive strength to the substrate, a range of 20,000 to 100,000 being particularly preferable.

[0022] Furthermore, the additives according to the invention, though can be used in any form of liquid and paste, may be premixed in advance as powder in the self-leveling material. A form as the powder and the moisture content contained in the powder are not restricted to particular ones; however, when the moisture content becomes larger, a solidification state and caking of the powder due to a hydration reaction with the hydraulic substance are generated; accordingly, the smaller, the more preferable.

[0023] The self-leveling materials to which the additives according to the invention can be applied are ones that

contain, as a hydraulic substance, mainly cements and gypsums; as fine aggregate and chemical admixture, various chemical admixtures such as various kinds of blast furnace slag, fly-ash and so on; and can be used as self-leveling materials. There is not at all the restriction on a composition thereof.

[0024] An addition amount of the additive according to the invention to the self-leveling material is, with respect to the hydraulic substance in the self-leveling material, in the range of 0.05 to 5% by weight (in terms of solid content of the copolymer) and preferably in the range of 0.1 to 3.0% by weight. Furthermore, the additives according to the invention can be used together with known additives. As the additives that can be used together, an anti-foaming agent, a viscosity improver, a waterproof agent, a retardant, an early strength agent, an accelerator, a water reducing agent, a high performance water reducing agent, a foaming agent, a gas forming agent, an AE agent and so on can be cited.

[0025]

[Examples]

Examples 1 through 10 and comparative examples 1 through 6

Pursuant to a method described in JP-A-07-223852, additives according to the invention and comparative additives shown Table 1 were manufactured. With these additives and furthermore, as comparative additives, a

commercially available naphthalene sulfonate-formalin condensate salt (product name: MIGHTY 100 manufactured by Kao Corporation, hereinafter abbreviated as NS) and a melamine sulfonic acid-formalin condensate salt (product name: MERUMENTO F-10 manufactured by SHOWA DENKO K.K., hereinafter abbreviated as MS), self-leveling materials having compositions shown in Table 2 were prepared. To ingredients other than the additives shown in Table 2, 90 parts by volume of water and the additive were added followed by blending at 300 rpm × 1 min with an stirrer with four blades. Thereafter, the obtained slurry was filled in a cylindrical cone having an inner diameter of 50 mm and a height of 50 mm. An amount of the additive is adjusted so that spreading after the pulling up may be 220 mm.

[0026]

[Table 1]

		Monomer composition of copolymer	Polymerization mole ratio	Molecular weight
Inventive product	1	Ally alcohol $(EO)_{65}$/sodium maleate	80/100	32000
	2	Methanol $(EO)_{65}$·methacrylic ester/sodium methacrylate	40/100	51000
	3	Methanol $(EO)_{70}$·methacrylic ester/methanol $(EO)_{9}$·methacrylic ester/sodium methacrylate	20/20/60	48000
	4	Methanol $(EO)_{120}$ · methacrylic ester/methanol $(EO)_{9}$·methacrylic ester/sodium methacrylate	4/20/76	55000
	5	Methanol $(EO)_{120}$·methacrylic ester/sodium methacrylate	35/100	57000
	6	Methanol $(EO)_{120}$·methacrylic ester/sodium methacrylate	25/100	45000
	7	Methanol $(EO)_{120}$·methacrylic ester/sodium methacrylate	10/100	41000
	8	Methanol $(EO)_{125}$ $(PO)_{10}^{*}$·methacrylic ester/sodium methacrylate	25/100	57000
	9	Methanol $(EO)_{180}$·methacrylic ester/sodium methacrylate	20/100	71000
	10	Methanol $(EO)_{250}$·methacrylic ester/sodium methacrylate	20/100	82000
Comparative product	1	Methanol $(EO)_{10}$·methacrylic ester/sodium methacrylate	60/100	32000
	2	Methanol $(EO)_{50}$·methacrylic ester/sodium methacrylate	40/100	40000
	3	Methanol $(EO)_{23}$·methacrylic ester/sodium methacrylate/sodium methacrylic sulfonate	30/10/60	35000
	4	Methanol $(EO)_{320}$·methacrylic ester/sodium methacrylate	20/100	91000

Note)*: Random adduct of EO and PO

[0027] In Table 1, EO denotes ethylene oxide, PO denotes propylene oxide, an addition mole number denotes an average addition mole number, and an average molecular weight of a copolymer is one obtained from a molecular weight according to gel permeation chromatography/polystyrene sodium sulfonate base.

[0028]

[Table 2]

Blended ingredient	Blending parts by weight
Ordinary Portland cement	90.0
Alpha hemihydrate gypsum	10.0
Blast furnace slag	50.0
#5 silica sand	100.0
Methyl cellulose*1	0.15
Anti-foaming agent*2	0.05
Potassium sulfate	0.5
Additive (powder)	Amount for adjusting the fluidity (amount shown in Table 4)

*1: Metrose 905H
(manufactured by Shin-Etsu Chemical Co., Ltd.)
*2: SN Foamer EX-3011
(manufactured by Sun Nobco Ltd.)

[0029] With self-leveling materials thereto above-mentioned various kinds of additives were added, according to a method below, the additives were evaluated. Results are shown in Table 4.

[0030] <Method of evaluation> In a frame having a length of 300 mm, a width of 300 mm and a height of 100 mm, ready-mixed concrete having a blending composition shown in Table 3 was charged with a thickness of 100 mm followed by hardening. On a concrete surface after the hardening, the above self-leveling material was poured in with a thickness of 20 mm and hardened as it is without applying trowel finishing. After cooling for 28 days, the surface smoothness, the adhesive strength and occurrence of cracks were evaluated according the methods below.

[0031] · Surface smoothness: judged by visual observation according to the following criteria.

◎ - extremely excellent in the smoothness

○ - smooth

Δ - slightly deficient in the smoothness

× - poor in the smoothness

・Adhesive strength: A surface of a test body was cut with a diamond cutter up to a concrete surface, a steel disc was adhered to a surface of the test body with an adhesive, a load when it was peeled by use of a Kenken type adhesion tester was obtained, and the adhesive strength was obtained from the following equation.

[0032]

[Suu 1]

$$\text{Adhesive strength} = \frac{\text{load when peeling occurred (kg)}}{\text{adhesion area of a disc (cm}^2\text{)}}$$

[0033] ・Occurrence of crack: visually observed.

[0034]

[Table 3]

Composition of underlying concrete

W/C (%)	s/a (%)	Unit amount (kg/m³)				
		C	W	SI	S	G
45	42.2	370	178	124	745	867

Materials used

W : tap water

C : center ordinary Portland cement, specific gravity = 3.16

SI : Blast furnace slag (specific surface area 6000), specific gravity = 2.89

S : river sand from Kino River, specific gravity = 2.56

G : crushed stone from Takarazuka, specific gravity = 2.60

s/a : sand/(sand + gravel) (volume ratio)

Chemical admixture : MIGHTY 2000 (manufactured by Kao Corporation), 5.5 kg/m³

[0035]

[Table 4]

		Additive for self-leveling agent		Surface smoothness	Adhesive strength (kg/cm^2)	Occurrence of crack
		Kind	Addition amount*			
Embodiment	1	Inventive product 1	1.3	○	14.5	None
	2	Inventive product 2	1.2	○	15.7	None
	3	Inventive product 3	1.2	○	15.6	None
	4	Inventive product 4	0.8	◎	18.0	None
	5	Inventive product 5	0.7	◎	18.7	None
	6	Inventive product 6	0.6	◎	19.0	None
	7	Inventive product 7	0.5	◎	19.5	None
	8	Inventive product 8	0.7	◎	18.1	None
	9	Inventive product 9	0.9	◎	17.5	None
	10	Inventive product 10	1.0	○	15.5	None
Comparative embodiment	1	Comparative product 1	1.7	×	10.2	Yes
	2	Comparative product 2	1.5	Δ	12.1	Yes
	3	Comparative product 3	1.7	Δ	11.2	Yes
	4	Comparative product 4	2.1	Δ	11.4	Yes
	5	NS	2.4	×	8.6	Yes
	6	MS	2.6	×	9.1	Yes

*: A weight percent to a total amount of ordinary Portland cement and gypsum

[0036]

[Effect of the Invention]

The self-leveling material thereto the additive according to the invention is added is excellent in the surface smoothness, high in the adhesive strength, and does not cause the occurrence of the crack; accordingly, troubles under construction and the endurance as a structure can be improved.